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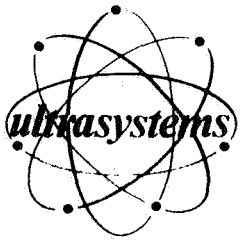
ULTRASYSTEMS , INC.
Irvine, California



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Ames Research Center

Robert W. Rosser, Technical Manager

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FOREWORD

This Annual Report describes the work performed by the Chemicals and Materials Research Department, Ultrasystems, Inc. under Contract NAS2-7981, "Study of Crosslinking and Degradation Mechanisms in Model Sealant Candidates". The investigations were carried out during the period from 15 September 1974 to 22 April 1977 by R. H. Kratzer, J. Kaufman, T. I. Ito, J. H. Nakahara, and K. L. Paciorek, project manager. This contract was administered by NASA Ames Research Center with Dr. Robert W. Rosser as technical manager.

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1. SUMMARY

The aim of this program was to determine on model compounds which type of heterocyclic ring is the most advantageous for curing sealants based on perfluoroalkylether chains. The study included the synthesis of specifically substituted materials and the evaluation of their stabilities in air, inert atmosphere, water, and Jet-A fuel at 235 and 325°C. Three heterocyclic ring systems were considered, namely, triazine, 1,2,4- and 1,3,4-oxadiazoles.

The major portion of the triazine and some of the 1,2,4-oxadiazole investigations have been completed under Phase I of this contract. The current phase included complete evaluation of the 1,3,4-oxadiazole system and the perfluoroalkylether substituted-1,2,4-isomer as well as determination of the effect of Jet-A and water on the previously studied perfluoroalkyl-1,2,4-oxadiazole and perfluoroalkylether triazine.

3-Perfluoroalkylether-5-perfluoro-n-heptyl-1,2,4-oxadiazole and its bisperfluoroalkylether analogue were obtained in 64 and 40% yields, respectively, using a three step synthesis. The 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole was prepared in 74% yield via reaction of 5-perfluoro-n-heptyltetrazole with perfluoro-n-octanoyl chloride; utilizing perfluoroalkylether acid chloride gave 2-perfluoro-n-heptyl-5-perfluoroalkylether-1,3,4-oxadiazole in 38% yield. The 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole was formed in 31% yield from the corresponding acyl fluoride and hydrazine hydrate followed by phosphorus pentoxide dehydration.

The perfluoroalkylether substituted triazine exhibited good stability to water even at 325°C and it was virtually unaffected by Jet-A fuel and air at 235°C.

3,5-Bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was also found to be stable to attack by water at 325°C; however, in air in the presence of Jet-A at 235°C the extent of degradation was in excess of 10%.

Its perfluoroalkylether analogue showed excellent thermal, thermal oxidative, and hydrolytic stability at 235 and 325°C as evidenced by practically quantitative recovery of the test samples. In the presence of Jet-A fuel at 235°C a low degree of degradation, ~4%, was observed.

2,5-Bis(perfluoro-n-heptyl)-1,3,4-oxadiazole in the absence of oxygen was stable up to 325°C in both pyrolytic and hydrolytic environments. In air at 235°C the results were not reproducible, indicating catalytic effects; at 325°C complete oxygen consumption accompanied by extensive material degradation took place. Its perfluoroalkylether analogue exhibited good oxidative stability at 235°C and was unaffected by Jet-A/air at this temperature; at 325°C in air some oxidation occurred as shown by 20% oxygen consumption and 96% starting material recovery. The effect was, however, significantly lower than in the case of the perfluoroalkyl substituted compound.

2. INTRODUCTION

Perfluoroalkylethers exhibit exceptionally good thermal stability in conjunction with low glass transition temperatures and fuel resistance. These properties render perfluoroalkylethers very attractive as potential candidates for advanced sealants required to function under extremes of temperatures in a fuel environment. For such an application it is of utmost importance to avoid introduction of weak links via curing and/or chain-extending operations. Furthermore, to develop a practical sealant system the crosslinking process should proceed readily, preferentially in a quantitative yield at relatively moderate temperatures. Ideally, it is desired for both of these conditions to be fulfilled; however, in real systems compromises have to be made.

To determine which type of an arrangement offers optimum properties for curing a perfluoroalkylether-based sealant system one of the approaches is to study models. Thus under this program a number of heterocyclic ring systems were synthesized and their stabilities evaluated under different environments and conditions.

3. RESULTS AND DISCUSSION

The objective of this investigation was to determine on specific model compounds the relative thermal, thermal oxidative, hydrolytic, and fuel stability of potential crosslinks useful for curing perfluoroalkylether elastomers. The perfluoroalkylethers available for the actual sealant development are composed of difunctional nitrile-terminated materials, obtained from diacid fluoride precursors (ref. 1). Consequently in any crosslinking and/or chain extension process either the reaction of the nitrile or the acid fluoride group can be utilized.

Under the first phase of this program (ref. 2,3) it was established that 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles and perfluoroalkylether-s-triazines exhibit desirable thermal, thermal oxidative, and hydrolytic stabilities. The ultimate application visualized for these systems is as fuel tank sealants; consequently, the effect of Jet-A fuel on these compounds at elevated temperatures had to be evaluated.

As noted above the 1,2,4-oxadiazole ring system offers a potential candidate for chain extension of perfluoroalkylether materials. Unfortunately, no data were available regarding the perfluoroalklyether-substituted analogues. The same was true for the 1,3,4-isomers. Accordingly, the feasibility and ease of formation of these compounds needed to be explored, especially since the ultimate objective of these studies is to utilize the most promising ring arrangements and the most direct processes leading to their formation in chain extending or crosslinking perfluoroalkylether polymers. In conjunction with the above requirement it was also of importance to determine how readily the "mixed" perfluoroalkyl, perfluoro-alkylether-oxadiazole can be formed. These types of compositions represent potential polymer systems utilizing both perfluoroalkyl and perfluoroalkylether segments.

3.1 MODEL COMPOUND SYNTHESIS

The 1,2,4-oxadiazole ring, when substituted by perfluoroalkyl groups, possesses very good thermal, thermal oxidative, and hydrolytic stability comparable to that of the perfluoroalkylether-substituted s-triazines. One would expect these characteristics to be even further enhanced by the presence of perfluoroalkylether substituents.

3-Perfluoroalkylether-5-perfluoro-n-heptyl-1,2,4-oxadiazole was prepared in an overall 64% yield by the general procedure of Brown and Wetzel (ref. 4):

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN$$

$$\downarrow NH_2OH$$

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=NOH$$

$$\downarrow n\text{-}C_7F_{15}COCl$$

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=N\text{-}O\text{-}C(O)\text{-}n\text{-}C_7F_{15}$$

$$\downarrow P_2O_5$$

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)\ C\begin{matrix}=N\text{-}O\\ \diagdown\quad\diagup\\ N=\end{matrix}C\text{-}n\text{-}C_7F_{15}$$

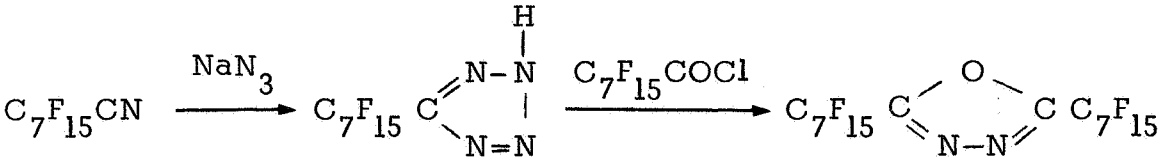
The analogous bis-perfluoroalkylether-1,2,4-oxadiazole was obtained in an overall 40% yield employing the above procedure and substituting a perfluoroalkylether acid chloride for the octanoyl chloride to give:

$$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)\ C\begin{matrix}=N\text{-}O\\ \diagdown\quad\diagup\\ N=\end{matrix}C\ CF(CF_3)OCF_2CF(CF_3)OC_3F_7$$

It has been reported that the 1,3,4-oxadiazole ring system is

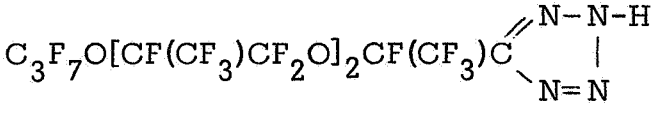
inherently more thermally stable than the isomeric 1,2,4-arrangement (ref. 5). In addition, the one step synthesis of 1,3,4-oxadiazoles utilizing the reaction of an acyl halide with a tetrazole (ref. 6) offers a definite advantage over the relatively tedious procedures required to produce the 1,2,4-materials. In view of the above considerations, investigation of the 1,3,4-oxadiazoles as potential crosslinking and/or chain extending "segments" appeared warranted.

The first member of this series, 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole was synthesized by the following sequence:



The tetrazole was prepared in 82% yield following the procedure of Finnegan and Boschan (ref. 7) and on treatment with perfluoro-n-octanoyl chloride, the desired oxadiazole was obtained in 90% yield.

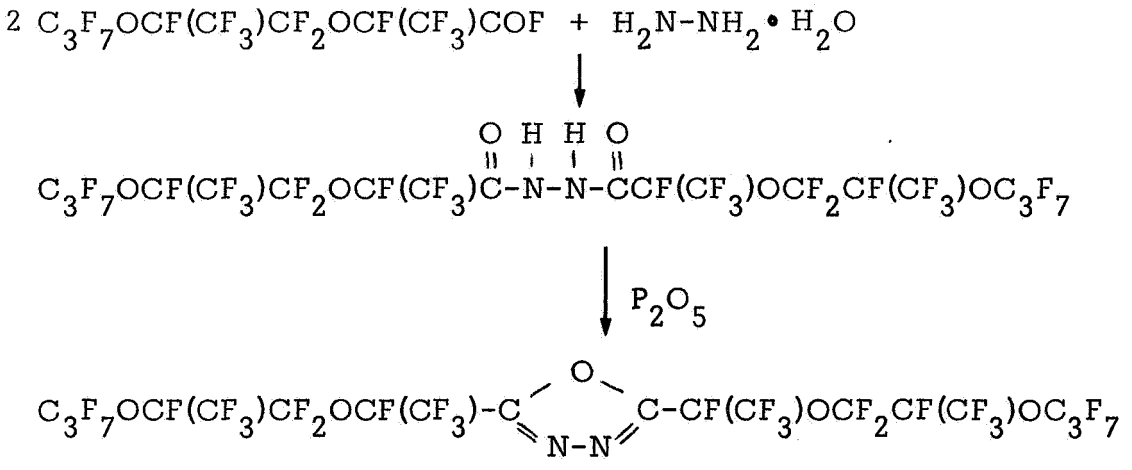
What appeared to be the perfluoroalkylether-substituted tetrazole,



was readily formed (in ~ 83% yield) from the respective nitrile and sodium azide; however, the subsequent reaction with acid fluoride, $C_3F_7OCF(CF_3)$-$CF_2OCF(CF_3)COF$, failed to give the oxadiazole. It was assumed that this failure was due either to the use of the acyl fluoride which was decomposed by reaction with the glass walls during the heating process or

to the unreactive nature of the $CF(CF_3)COX$ arrangement. Neither of these assumptions was correct since the perfluoroalkylethertetrazole, when reacted with perfluoro-n-octanoyl chloride, formed only traces of the 2-perfluoro-n-heptyl-5-perfluoroalkylether-1,3,4-oxadiazole admixed with unidentified polychlorinated materials. The latter compound was, however, obtained in ~47% yield from the reaction of the perfluoro-n-heptyltetrazole with the perfluoroalkylether acid chloride. Consequently, it has to be deduced that the perfluoroalkylethertetrazole is responsible for the observed lack of reaction.

2,5-Bis(perfluoroalkylether)-1,3,4-oxadiazole was finally obtained in 31% yield, using the procedure of Chambers and Coffman (ref. 8), i.e.:



3.2 DEGRADATION STUDIES

3.2.1 Jet-A Fuel Investigations

One of the requirements of the program is the evaluation of the thermal stability of the model sealant system in Jet-A fuel. A given fuel consists of a number of components the nature and relative concentration of which could very well be affected by the model sealant; thus these

had to be determined quantitatively. To facilitate the GC-MS analyses the fuel was first fractionated using vacuum line techniques. The fractionation data for the fuel and fuel model sealant mixtures are given in Table I. It was found that neither the nature nor component distribution varied for the Jet-A fuel when subjected to the heat treatment; consequently, only the GC-MS of the material heated in air atmosphere at 235°C is given (see Table II). Apparently, the temperatures up to 325°C do not produce significant pyrolytic degradations, which is to be expected. In air at 235° oxidation does occur as shown by the complete oxygen consumption and the products formed listed in Table III. However, since the quantity of oxygen available was very small (5.9 mg) as compared to the quantity of Jet-A employed ($\sim$1 g), the extent of oxidation as evidenced by carbon dioxide, carbon monoxide, and carbonyls formation was also very low and the nature of the Jet-A was essentially unchanged. The oxygen-containing volatiles formed accounted for $\sim$ 10% of the oxygen consumed. It is quite plausible that at least 50% of the oxygen consumed was transformed into water (which would correspond to $\sim$ 0.15 mmol). It is mainly the water in conjunction with the other oxygenated species which provide the degradative environment of a fuel system.

3.2.2 Perfluoroalkylether-s-triazine, $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$

Degradations performed on the perfluoroalkylether-s-triazine during Phase I of this program (ref. 2,3) showed this material to exhibit exceptional thermal, thermal oxidative, and hydrolytic stability. At that time the hydrolytic stability was determined only at 235°C; it was thus of interest to evaluate the effect of water at temperatures higher than 235°C. As can be seen from Table IV 95.5% of the starting material was recovered unchanged. The three main products formed were

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH_2$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$. The recovery of the nitrile after the treatment at 325°C in the presence of water is very surprising. Inasmuch as the nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, and the corresponding amide were the major species formed, one is tempted to speculate that the triazine first dissociates thermally and this process is then followed by hydrolysis of the produced nitrile.

It is apparent from the data presented in Table IV that the triazine was only slightly affected by the exposure to Jet-A fuel/air at 235°C. Based on its stability in air and water up to 325°C, this result was to be expected.

3.2.3 3,5-Bis(perfluoro-n-heptyl)-1,2,4-oxadiazole

3,5-Bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was previously subjected to nitrogen and air at 325°C as well as to nitrogen/water atmospheres at 235°C (ref. 3,2). The effect of higher temperatures on its stability in the presence of water was of particular interest since the absence of hydrolysis at 235°C in water was surprising in view of the $-CF_2-C\overset{N}{\underset{N}{=}}$ arrangement present in the 1,2,4-oxadiazole ring. This same grouping is a component of the s-triazine ring and must be in this combination responsible for the hydrolytic instability of tris(perfluoro-n-heptyl)-s-triazine (ref. 3,2). It is obvious from the data presented in Table V that even at 325°C, the extent of degradation of 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was very minor. This unexpected finding is so far unexplained.

The Jet-A fuel/air at 235°C presented a much more severe degradative environment for the 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole than any of the other treatments investigated. The oxadiazole recovered corresponded to 73% of the starting material; adding all the other fluorinated

compounds identified and quantitated brings this figure to 82%. A portion of the unaccounted for 18% are fluorinated moieties which could not be detected or separated using the techniques employed; in addition the experimental error in actual determinations will also contribute to the material balance discrepancy. The major product formed was the amide, $n\text{-}C_7F_{15}CONH_2$. From the data given in Table V it can be calculated that the quantity of 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole employed was 1.03 mmol and as noted in Section 3.2.1, the water from oxidation of the fuel is of the order of ~0.15 mmol; consequently, the quantity of the amide theoretically possible is in reasonable agreement with the 6.6% of $n\text{-}C_7F_{15}CONH_2$ produced. Based on these findings it is apparent that this oxadiazole is susceptible to hydrolysis provided a solubilizing medium is present. This is in agreement with Dr. Tamborski's investigations (ref. 9) which showed that in the presence of tetrahydrofuran and water, 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole undergoes extensive hydrolysis at 100°C. These results would indicate that if the polymer system containing the perfluoroalkyl-1,2,4-oxadiazole linkage is essentially insoluble in Jet-A or any other fuel or solvent, no hydrolytic degradation should occur since water alone is ineffective.

3.2.4 3,5-Bis(perfluoroalkylether)-1,2,4-oxadiazole

The results of the studies performed on the perfluoroalkylether-substituted 1,2,4-oxadiazole are summarized in Table VI. Under all the conditions, with the exception of the air-Jet-A treatment, ~ 99% of the starting material was recovered unchanged. The effect of air at 235 and 325°C was virtually the same, based on starting material recovery and oxygen consumption. This is unexpected and may be attributable to the presence of a small quantity of an impurity. From the air-Jet-A exposure at 235°C, 92.3% of the starting material was recovered intact; the detected

and quantitated products, however, accounted for only ~4% of the material loss. In view of the experimental difficulties associated with physically separating the Jet-A fuel from the (liquid) test sample, it is quite plausible that the actual extent of degradation is better represented by the amount of products formed than by the quantity of starting material recovered since no other indication of degradation such as discoloration could be observed. In the case of 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole, this argument cannot be made because the starting material is a solid which could be fairly readily separated from Jet-A fuel. In addition, the dark brown discoloration observed in this test indicated that degradation was extensive.

3.2.5 2,5-Bis(perfluoro-n-heptyl)-1,3,4-oxadiazole

The results of the studies performed on the 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole are summarized in Table VII. It can be seen that in the absence of oxygen the material exhibited good stability up to 325°C. This was true both in inert atmospheres and in the presence of water. These investigations were performed in argon to allow the detection of nitrogen since the latter was postulated as a breakdown product in the 1,3,4-oxadiazoles under electron impact (ref. 10, 11). Thus it was of importance to determine whether this degradation path is also present under thermal or hydrolytic conditions. In none of the tests was nitrogen evolution observed, which is in agreement with thermal breakdown findings of others (ref. 11). After subjecting the sample to argon/water environment at 235°C the only products formed in the volatiles were small quantities of carbon dioxide and fluorohydrocarbons (most likely from further degradation of R_fCN and related precursors), whereas in the involatile residue traces of R_fCONH_2 were present as shown by a weak infrared band at 5.9 μ. No amide was detected by gas chromatography.

Under analogous conditions but at 325°C, the results were virtually identical. In the absence of water at 325°C perfluoro-n-octanonitrile was the only constituent of the volatiles. Thus it can be deduced that water as such has no degradative action upon 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole. The products formed are derived from the hydrolysis of the nitrile initially produced. This behavior is analogous to that observed for the 1,2,4-oxadiazole.

Contrary to the behavior of the 1,2,4-analogue the 1,3,4-oxadiazole was found to be oxidatively unstable. No reproducible results could be obtained in air at 235°C. Using an identical sample of starting material in one test resulted in complete oxygen consumption together with production of volatiles. In another test, employing a much larger relative quantity of oxygen, virtually no degradation took place. This would then indicate that in the first test a trace of impurity, possibly present in the reaction vessel, catalyzed the decomposition. The susceptibility of the 1,3,4-oxadiazoles to nuclephilic attack was demonstrated by Brown and Cheng (ref. 12); on the other hand, this isomer is supposed to exhibit better thermal stability than the 1,2,4-isomer (ref. 5). The low oxidative stability was clearly shown by the exposure to air at 325°C when all the available oxygen was consumed and only 60% of the starting material was recovered. The products formed are listed in Table VIII. It should be noted that SiF_4, BF_3, and part of CO_2 are derived most likely from the reaction of COF_2 and R_fCOF species with the walls of the ampoule. The unidentified products consisted of perfluoroalkyl carbonyls, R_fCOF (identified by infrared absorption at 5.27 μ and mass spectral abundances at m/e = 97, 47, and 66), perfluoroalkyl acid anhydrides $(R_fCO)_2O$ (identified by infrared absorptions at 5.38 and 5.52 μ) and a completely unknown compound which exhibited strong absorptions in the infrared at 6.18 and 6.31 μ. The latter material was present also in the involatile residue, which

would indicate that it is a relatively high molecular weight species. The relative quantity of the nitrile, $C_7F_{15}CN$, produced was much higher than in the argon test performed at the same temperature which shows clearly that oxygen-initiated ring opening is operative here. Inasmuch as all the oxygen was consumed, it is safe to assume that in the presence of sufficient air (oxygen) no oxadiazole would be recovered.

In view of the above findings it was concluded that 2,5-bis-(perfluoro-n-heptyl)-1,3,4-oxadiazole and related compositions are not suitable for the visualized sealant applications. Consequently no studies involving the Jet-A fuel were carried out.

3.2.6 2,5-Bis(perfluoroalkylether)-1,3,4-oxadiazole

As discussed above the oxidative stability of the 1,3,4-oxadiazole ring system when substituted by perfluoroalkyl groups was found to be poor. In view of the tremendous difference in reactivity of the perfluoro-alkyl- and perfluoroalkylether-substituted s-triazines, which was determined under the first phase of this program, it seemed reasonable to assume that similar effects might also be operative here. It has been discussed previously and it is being reemphasized again that it is not the ether function which is responsible for this behavior but the steric hindrance of the $-CF(CF_3)-$ arrangement adjacent to the ring. Consequently, 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole was synthesized and subjected to degradative testing. The results of these investigations are compiled in Table IX and the nature and relative proportion of the products formed under the different investigations are given in Table X.

It is apparent from these data that at 235°C under oxidizing, hydrolytic, and fuel environments, very little decomposition took place as shown by starting material recovery and the degradation products

found. Based on the latter value and due to the difficulty in separating the oxadiazole from Jet-A fuel it is most likely that the actual degree of degradation is lower than that reported in Table IX. Oxidatively, however, the 1,3,4-oxadiazole was not as stable as its 1,2,4-isomer (compare data presented in Tables VI and IX); yet, it was definitely much more stable than the perfluoro-n-heptyl-substituted analogue. Among the products listed (see Table X) the nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, originates most likely from dissociation of the oxadiazole. The hydrogenated fluorocarbons are probably produced from further degradation of the nitrile to acid fluorides and from the decomposition of the other dissociation components. One of the operative processes is presented below:

$$R_fOCF(CF_3)COF \xrightarrow{Si\text{-}OH} R_fOCF(CF_3)COOH + SiF_4$$

$$R_fOCF(CF_3)COOH \xrightarrow{\Delta} R_fOCF(CF_3)H + CO_2$$

The presence of silicon tetrafluoride and carbon dioxide supports this scheme. The finding of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]OCF_3$ is unexpected; on the other hand, if produced, this species would indicate a high degree of stability of this ring system.

Based on the above findings it can be concluded that the 1,3,4-oxadiazole ring system can be rendered relatively oxidatively stable by suitable substitution. Apparently, materials with $-CF(CF_3)-$ group next to the 1,3,4-oxadiazole ring offer comparable, if not better, stability in the fuel environment than the 1,2,4 compounds. Since perfluoroalkyl-ethers derived from perfluoropropene oxide are the current candidates

for the sealant applications, the employment of the 1,3,4-oxadiazole as the crosslinking segments can be considered although in view of the oxidative behavior at elevated temperatures might not be as desirable as the 1,2,4-ring arrangement.

4. EXPERIMENTAL DETAILS AND PROCEDURES

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B) or under a nitrogen by-pass. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means. The perfluoroalkylether nitrile and acid fluoride obtained from the Air Force Materials Laboratory were employed without purification due to the relatively small samples available and the likelihood of material loss on purification.

Infrared (IR) spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Molecular weights were determined in hexafluorobenzene solution using a Mechrolab Model 302 vapor pressure osmometer. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectrometric analyses were performed using a CEC Model 21-620 mass spectrometer and a DuPont spectrometer 21-491B coupled to a data acquisition and processing system. The latter instrument was employed both in GC-MS and batch modes.

4.1 MODEL COMPOUND SYNTHESIS

Preparation of 3-perfluoroalkylether-5-perfluoro-n-heptyl-1,2,4-oxadiazole, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[C_2N_2O]$-n-$C_7F_{15}$

Under nitrogen by-pass to a stirred solution of hydroxylamine hydrochloride (0.59 g, 8.49 mmol) in dry methanol (10 ml) was added at 22-25°C sodium methoxide (8.26 mmol in 5 ml methanol). Into this solution was then introduced $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN$ (5.02 g, 7.81 mmol), again at 22-25°C. After stirring for 2 hr at room temperature, methanol was taken off under reduced pressure and the resulting mixture

(white solid suspended in a clear liquid) was taken up in Freon 113, filtered and evaporated under reduced pressure. The remaining involatile, clear liquid, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=NOH$, 4.32 g (81.8% yield) was employed without further purification in the next step.

Under nitrogen by-pass to a stirred solution of the amidoxime (4.07 g, 6.02 mmol) in tetrahydrofuran (20 ml) was added slowly at 0°C perfluoro-n-octanoyl chloride (2.61 g, 6.03 mmol) in tetrahydrofuran (7 ml). After completing the addition, the reaction mixture was stirred for 1 hr at 0°C, then 2 hr at room temperature. Subsequently, tetrahydrofuran was removed under reduced pressure leaving a viscous liquid (5.82 g, 90.2% yield); this material exhibited an infrared spectrum containing bands characteristic for the expected structural arrangement, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=N-O-C(O)-n-C_7F_{15}$.

A mixture of this O-perfluoroalkylether-perfluoro-n-octanoyl-amidoxime (5.82 g, 5.43 mmol) and phosphorus pentoxide (7.10 g, 50.0 mmol) was heated under nitrogen by-pass for 10.3 hr at 230°C. Subsequently, the oxadiazole was distilled from the reaction mixture under reduced pressure. Redistillation gave the pure product (4.99 g, 64% overall yield) bp 84-88°C /1 mm Hg.

Anal. Calcd. for: $C_{20}F_{38}O_4N_2$: C, 22.79; F, 68.48; N, 2.66; O, 6.07; MW, 1054.17.

Found: C, 22.97; F, 67.85; N, 2.72; MW, 1070.

The mass spectral breakdown pattern given in Table XI is in agreement with the assigned structure.

Preparation of 3,5-bis-perfluoroalkylether-1,2,4-oxadiazole, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

Under nitrogen by-pass to a stirred solution of the amidoxime, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=NOH$, (9.20 g, 13.61 mmol) in

tetrahydrofuran (25 ml) was added slowly at 0°C $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COCl$ (7.01 g, 13.62 mmol) in tetrahydrofuran (8 ml). After completing the addition, the reaction mixture was stirred for 1 hr at 0°C, then 2 hr at room temperature. Subsequently, tetrahydrofuran was removed under reduced pressure giving the O-perfluoroalkylether-perfluoroalkylether-acyl-amidoxime, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)C(NH_2)=N-O-C(O)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, as a viscous liquid (14.32 g, 91.2% yield).

A mixture of the thus obtained O-perfluoroalkylether-perfluoroalkylether-acyl-amidoxime (14.32 g, 12.41 mmol) and phosphorus pentoxide (16.0 g, 112.7 mmol) was heated under nitrogen by-pass for 12 hr at 210-216°C. Subsequently, the oxadiazole was distilled from the reaction mixture under reduced pressure. Redistillation gave the pure product (6.13 g, 40% overall yield), bp 120-122°C/7.2 mm Hg.

Anal. Calcd. for $C_{21}F_{40}O_6N_2$: C, 22.20; F, 66.89; N, 2.47; O, 8.45; MW, 1136.18.

Found: C, 22.59; F, 66.98; N, 2.90; MW, 1200.

The mass spectral breakdown pattern given in Table XI is in agreement with the assigned structure.

Preparation of perfluoro-n-octanoyl chloride

A mixture of 100.05 g (241.6 mmol) of perfluoro-n-octanoic acid and 58.96 g (290.4 mmol) of isophthaloyl chloride was heated under nitrogen by-pass at 85-96°C for 3 hr; this was followed by distillation at ca 60 mm Hg which gave 52.3 g (50% yield) of crude perfluoro-n-octanoyl chloride. Redistillation afforded the pure product, 45.52 g (43.6% yield), bp 75-77°C/110 mm Hg.

Preparation of perfluoroalkylether acid chloride, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COCl$

A mixture of perfluoroalkylether acid, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2H$, (12.98 g, 26.16 mmol, obtained by water hydrolysis of the corresponding acid fluoride) and 11.73 g (54.67 mmol) of isopthaloyl chloride was heated under nitrogen by-pass at 110-120°C for 8 hr. Distillation under reduced pressure gave 11.39 g (84.6% yield) of a water clear distillate, bp 82-84°C/129 mm Hg.

Preparation of perfluoro-n-heptyltetrazole

A mixture of perfluoro-n-octanonitrile (24.94 g, 63.93 mmol), dimethylformamide (35 ml), ammonium chloride (3.76 g, 70.28 mmol), and sodium azide (4.53 g, 69.68 mmol) was heated under nitrogen by-pass at 100-103°C for 14 hr. The initially present two layers became a slightly orange single phase with solid at the bottom of the flask. Dimethylformamide was then removed in vacuo to yield a pasty residue which was only partially soluble in water (75 ml), but dissolved on addition of 20% HCl (75 ml). The organic material was extracted with ether, washed with 20% HCl and water and dried over anhydrous $MgSO_4$. Evaporation of ether yielded 30.10 g (98.3% yield) of crude n-perfluoroheptyltetrazole. This material was crystallized from chloroform affording 15.63 g (51% yield) of product, mp 88-89°C. On evaporation of the mother liquor an additional 9.45 g of the tetrazole was obtained bringing the total yield to 81.9%.

Preparation of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole

A mixture of perfluoro-n-heptyltetrazole (10.01 g, 22.85 mmol) and perfluoro-n-octanoyl chloride (11.04 g, 25.52 mmol) was heated under a nitrogen by-pass at 89-93°C for 4.7 hr; at 104-112°C for 38.6 hr and finally at 121-125°C for 24 hr. The product was purified by dissolving it in ether followed by washing with sodium carbonate solution

and water. The residue left on removal of ether was crystallized from ether-ethanol giving 16.55 g (89.9% yield) of 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole, mp 33-34°C.

Anal. Calcd. for $C_{16}F_{30}N_2O$: C, 23.84; F, 70.70; N, 3.48.
Found: C, 23.98; F, 70.98; N, 2.82.

The mass spectral breakdown pattern given in Table XII is in agreement with the assigned structure.

Preparation of perfluoroalkylethertetrazole, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)(CN_4H)$

A mixture of perfluoroalkylether nitrile, $C_3F_7O[CF(CF_3)CF_2O)_2CF(CF_3)CN$, (4.99 g, 7.77 mmol), ammonium chloride (0.57 g, 10.65 mmol), sodium azide (0.67 g, 10.31 mmol) and dimethylformamide (10 ml) was heated under nitrogen by-pass for 18 hr at 99-110°C. The initially present two layers gradually became a single phase within ca 90 min. The dimethylformamide was subsequently removed in vacuo. The viscous residue was treated with 20% HCl (20 ml) and the resulting mixture extracted with ether (4 x 25 ml). The combined extracts were washed with 20% HCl (2 x 15 ml), water (3 x 15 ml) and dried over anhydrous magnesium sulfate. The viscous oil, which remained after solvent removal was distilled to give a viscous liquid (4.44 g, 83.4% yield), bp 102-104°C/0.01 mm Hg; its infrared spectra was consistent with the assigned structure.

Attempted preparation of 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

A mixture of perfluoroalkylether tetrazole, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[CN_4H]$, (3.46 g, 5.04 mmol) and perfluoroalkylether acid fluoride, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$, (3.23 g, 6.49 mmol) together with

approximately 0.1 g of glass beads (Perkin-Elmer 45/80 mesh) was heated under nitrogen by-pass at 90.5-95.5°C for 2.4 hr and at 78.5-83°C for 43.2 hr. The resulting dark colored liquid was subsequently distilled at < 0.01 mm Hg. Three fractions: bp 34-44°C, 44-68°C, and 68-83°C were obtained. Based on the infrared spectral analyses these consisted respectively of perfluoroalkylether acid, a mixture of the acid and starting tetrazole and the tetrazole. No oxadiazole appeared to have been formed.

Attempted preparation of 2-perfluoro-n-heptyl-5-perfluoroalkylether-1,3,4-oxadiazole, n-$C_7F_{15}[C_2N_2O]CF(CF_3)(OCF_2CF(CF_3))_2OC_3F_7$

A mixture of perfluoroalkylether tetrazole (1.09 g, 1.59 mmol) and perfluoro-n-octanoyl chloride (1.07 g, 2.47 mmol) was heated under nitrogen by-pass for 67.2 hr at 84.5-90.5°C and for 68 hr at 96-106°C. Distillation of the product gave three fractions: bp 34-49°C/44-39 mm Hg (trace); 45-51°C/39-33 mm Hg (0.2 g), and 77-83°C/3-1 mm Hg (0.68 g) were obtained. Approximately half of the liquid still remained in the distillation flask (0.94 g). Absence of bands at 6.35, 6.42μ in the infrared spectrum indicated that no oxadiazole was formed. Based on mass spectral analysis: fraction No. 2 was composed largely of n-$C_7F_{15}COCl$, fraction No. 3 was a mixture of the acid chloride with the desired oxadiazole, whereas the residue contained the oxadiazole mixed with what appeared to be a dichloro-compound or compounds.

Preparation of 2-perfluoro-n-heptyl-5-perfluoroalkylether-1,3,4-oxadiazole, n-$C_7F_{15}[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

A mixture of perfluoro-n-heptyltetrazole (3.03 g, 6.92 mmol) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COCl$ (3.69 g, 7.17 mmol) was heated under nitrogen by-pass at 115-118°C for 100 hr. The prolonged heating was required in view of the low reactivity of the perfluoroalkylether acid

chloride. The progress of reaction was monitored by cooling the reaction mixture and observing the crystallization of the unreacted tetrazole. The product mixture was subsequently distilled at 25 mm Hg; the fractions, bp 105-114°C and 114-126°C (2.91 g, 47% yield), based on infrared spectral analysis consisted of the desired oxadiazole. The fraction bp 105-114°C was dissolved in Freon 113, washed with sodium bicarbonate, water and dried over magnesium sulfate. Vacuum distillation yielded pure $n\text{-}C_7F_{15}(C_2N_2O)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, bp 118-121°C at 25 mm Hg.

Anal. Calcd. for $C_{17}H_{32}O_3N_2$: C, 22.99%; F, 68.45%; O, 5.40%; N, 3.15%; MW, 888.15.

Found: C, 23.29%; F, 68.36%; N, 3.39%, MW, 930.

Its infrared and mass spectra (see Table XII) were consistent with the assigned structure.

Preparation of 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

Under nitrogen by-pass to a stirred solution of $C_3F_7OCF(CF_3)$-$CF_2OCF(CF_3)COF$ (7.17 g, 14.39 mmol) in benzene (15 ml) was added hydrazine hydrate (0.73 g, 14.58 mmol). After stirring for 1.5 hr the mixture was refluxed for 4 hr with a water eliminator attached. Subsequently the mixture was cooled and decanted; the product dissolved in Freon-113 and filtered. To the solid residue, remaining after Freon-113 removal in vacuo, was added phosphorus pentoxide (16.8 g, 118 mmol). The solid mixture was then heated under nitrogen by-pass for 2 hr at 250°C. The volatiles, (3.54 g, 50.7% yield) bp 76-67°C/2.9-1 mm Hg, based on infrared spectral analysis consisted of the oxadiazole admixed with a carbonyl group-containing material. The product was thus dissolved in Freon-113 washed with water, 5% sodium bicarbonate solution and dried over magnesium sulfate. Distillation gave pure 3,5-bis(perfluoroalkylether)-1,3,4-oxadiazole (2.16 g, 31% yield) bp 102-104°C/9 mm Hg.

Anal. Calcd. for $C_{18}F_{34}N_2O_5$: C, 22.29; F, 66.58: N, 2.89; O, 8.25; MW, 970.16

Found: C, 21.98; F, 66.89; N, 3.21%; MW, 950.

Its mass spectrum given in Table XII was consistent with the assigned structure.

4.2 DEGRADATION STUDIES

The degradation investigations were performed in sealed ampoules of ca 50 ml volume, unless otherwise specified, over a period of 48 hr at 235 and 325°C. The media studied were nitrogen or argon, air, nitrogen or argon/water, and Jet A-fuel. The quantities of material employed were between 0.5-1.0 g, whereas the gas pressures used were ca 350 mm Hg at room temperature. In the experiments involving water and Jet-A fuel these materials were weighed into the ampoules. At the conclusion of an experiment the ampoules were cooled in liquid nitrogen and were opened into the vacuum system. The liquid nitrogen noncondensibles were measured and determined by mass spectrometry. The liquid nitrogen condensibles, which were volatile at room temperature, were fractionated from a warming trap through -23, -78°C into a liquid nitrogen cooled trap. Each fraction was measured, weighed and analyzed by infrared spectroscopy and mass spectrometry. The residue itself was weighed and subjected to gas chromatography, infrared spectral analyses, and differential thermal analysis.

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TABLE I

SUMMARY OF THERMAL. OXIDATIVE DEGRADATIONS OF JET-A

FUEL AND MODEL SEALANT JET-A FUEL MIXTURES [a]

Model Sealant		Jet-A	Temp	Atm	Involatile Residue					Condensible Volatiles					
					Total	CF-layer		CH-layer		-23°C		-78°C		LN_2	
Identification	Amount mg	Amount mg	°C		mg	mg	%[b]	mg	%[c]	mg	%[c]	mg	%[c]	mg	%[c]
-	-	971.6	-	-	604.2	-	-	604.2	62.2	201.0	20.7	148.1	15.2	3.7	0.4
-	-	1016.6	325	N_2	742.9	-	-	742.9	73.5	200.3	19.8	53.8	5.3	1.9	0.2
-	-	1016.2	235	Air	724.7	-	-	724.7	71.3	219.0	21.5	57.6	5.7	1.9	0.2
$(n\text{-}C_7F_{15})_2(C_2N_2O)$ [l]	832.2	847.0	235	Air	1037.1	745.8[d]	89.6	291.3[e]	34.4	528.1[f]	58.0 ?	100.9	11.9 ?	5.6	0.7 ?
$[R_fOR_fOCF(CF_3)]_3C_3N_3$ [g]	500.2	1091.1	235	Air	1319.5	479.1[h]	95.8	840.4[i]	73.9[j]	215.0	19.7 ?	49.4	4.5 ?	13.7	1.2 ?
$[R_fOR_fOCF(CF_3)]_2[C_2N_2O]$ [l]	896.1	920.2	235	Air	1491.5	834.0[k]	93.1	647.5	70.4	241.2	26.2	57.6	6.3	2.7	0.3
$[R_fOR_fOCF(CF_3)]_2[C_2N_2O]$ [m]	632.5	667.3	235	Air	914.9	591.1	93.5	323.8	48.5	327.8	49.1	42.0	6.3	4.7	0.7

a) All these degradations were performed in sealed tubes of ca 50 ml volume over a period of 48 hr under the specified conditions of atmosphere and temperature. The pressures employed were ca 350 mm at room temperature. b) Weight percent of model sealant. c) Weight percent of the Jet-A fuel originally employed. d) This sample contained 569 mg of oxadiazole and 55 mg of $n\text{-}C_7F_{15}CONH_2$; the remainder being entrapped Jet-A fuel. e) This fraction contained 0.3 mg of oxadiazole. f) This fraction contained 37.0 mg of oxadiazole. g) The compound tested was $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$. h) This includes also a small quantity of black insoluble solid; however, the ether triazine accounted for the bulk > 90% of the sample. i) This fraction contained 33.6 mg of $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$. j) This value does not include the 33.6 mg of the triazine found in the hydrocarbon layer. k) This fraction contained 98% of $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$; the remainder being the amides, the nitriles, and the hydrogen terminated perfluoroalkylethers. l) This was the 1,2,4-isomer. m) This was the 1,3,4-isomer.

TABLE II

GAS CHROMATOGRAPHIC ANALYSES OF JET-A FUEL SUBJECTED TO 235°C IN AIR FOR 48 HR[a]

Involatiles		-23°C Frac		-78°C Frac		Peak Identification
r.t.[b]	Area[c]	r.t.[b]	Area[c]	r.t.[b]	Area[c]	
				2.5	0.2	C_6H_{14}
				2.6	0.2	C_6H_{14}
				2.8	1.0	n-C_6H_{14}
				3.2	1.1	c-C_6H_{12}
				3.8	6.8	C_7H_{16}, benzene
				4.0	8.2	c-C_7H_{14}, C_7H_{16}
				4.2	6.8	C_7H_{16}
4.9	T[d]	4.9	T	4.4	21.0	n-C_7H_{16}
5.4	0.1	5.5	0.1	4.9	37.0	c-C_7H_{14}
		5.7	T	5.1	0.3	
		6.1	T	5.5	1.2	
6.6	0.2	6.6	0.9	5.8	43.4	C_8H_{18}
6.9	0.2	6.9	1.2	6.1	39.0	c-C_8H_{16}
7.6	0.4	7.5	4.8	6.6	75.1	n-C_8H_{18}
8.5	0.1	8.5	1.0	7.5	90.8	C_9H_{20}
8.7	1.0	8.7	10.5			C_9H_{20}
9.6	0.9	9.6	17.3	8.1	89.0	C_9H_{20}
9.8	0.8	9.8	11.9	8.3	1.8	C_9H_{20}
10.4	1.0	10.4	14.3	8.7	34.9	C_9H_{20}
10.8	4.3	10.8	54.4	9.0	66.9	n-C_9H_{20}
11.4	0.6	11.5	5.9	9.6	9.9	
11.9	8.9	12.0	49.9	9.9	30.8	$C_{10}H_{22}$
12.2	0.2	12.3	17.1	10.1	9.3	$C_{10}H_{22}$
12.9	13.1	12.9	69.9	10.6	32.0	$C_{10}H_{22}$
13.2	5.6	13.3	2.7			$C_{10}H_{22}$
13.7	8.9	13.7	26.7	11.2	8.2	C_3-benzene
14.2	28.3	14.3	102.4	11.5	13.1	n-$C_{10}H_{22}$
14.7	0.5	14.7	3.2	11.9	1.8	C_4-benzene
15.1	7.7	15.1	29.9	12.1	0.9	$C_{11}H_{24}$
15.6	0.8	15.6	12.8			C_4-benzene
16.0	0.3	15.9	2.1	12.8	0.9	
16.2	0.8	16.2	1.1	13.0	0.9	$C_{11}H_{24}$
16.6	9.1	16.6	3.7			$C_{11}H_{24}$
17.1	0.3	17.0	1.1	13.5	0.3	C_4-benzene
17.7	76.8	17.7	86.4	13.9	0.5	n-$C_{11}H_{24}$

TABLE II - Cont'd.

Involatiles		-23°C Frac		-78°C Frac		Peak Identification
r.t.[b]	Area[c]	r.t.[b]	Area[c]	r.t.[b]	Area[c]	
18.3	1.1	18.2	2.1	14.4	T	C_4-benzene
18.8	11.7	18.8	12.3	14.8	0.1	C_5-benzene, $C_{10}H_{16}O$
19.6	15.5	19.6	9.0			$C_{12}H_{26}$
19.8	3.7	19.8	0.6			$C_{12}H_{26}$
20.6	0.5	20.6	0.7			c-$C_{12}H_{24}$
21.1	84.8	21.0	17.6			n-$C_{12}H_{26}$
21.6	22.4	21.5	4.0			$C_{13}H_{28}$
22.1	2.7	22.0	0.7			
22.4	2.7	22.3	0.4			c-$C_{13}H_{26}$?
22.9	1.1	22.8	0.3			$C_{13}H_{28}$
23.2	1.1	23.1	0.3			$C_{13}H_{28}$
23.5	33.6	23.4	1.7			$C_{14}H_{30}$
24.3	75.7	24.2	2.7			n-$C_{13}H_{28}$
24.9	2.1					$C_{14}H_{30}$
25.8	4.8	25.6	0.1			$C_{14}H_{26}$ (c-?)
26.3	7.5					$C_{14}H_{30}$, $C_{14}H_{28}$ (c-?)
26.7	12.0	26.6	0.1			$C_{15}H_{32}$
27.3	52.3	27.2	0.2			n-$C_{14}H_{30}$
28.3	0.5					
28.7	0.8					
29.2	8.8					$C_{16}H_{34}$
30.1	18.9					n-$C_{15}H_{32}$
31.7	2.8					$C_{17}H_{36}$
32.8	3.7					n-$C_{16}H_{34}$
34.2	0.5					
35.6	0.7					

a These materials were examined under the following conditions: Column stainless steel 10' x 1/8" 4% OV-101 on Chromosorb G, detector a 43% split into F.I., He flow 38 ml/min, column temperature: 50 to 240°C programmed at 4°C/min.

b Retention time, min.

c This is a liquid fraction; area is given in square inches x attenuation per microliter of sample.

d < 0.05 $in^2/\mu l$.

TABLE III

PRODUCTS FORMED ON THERMAL OXIDATIVE DEGRADATION OF JET-A FUEL AT 235°C

Compound	Weight percent of Jet-A used
CO	0.028
CO_2	0.035
CH_4	T
SO_2	0.01
COS	T
C_2- and C_3-hydrocarbons	0.003
Acetaldehyde	0.005
Butyraldehydes	0.004
Acetone	0.015
Methyl ethyl ketone	0.005
2-Pentanone	0.004
Methyl formate	T
Ethyl formate	T
Methane	0.001
Ethane	T
Ethylene	T
Propane	T
Propylene	T
Cyclopropane	T

T = < 0.0005% by weight

TABLE IV

SUMMARY OF DEGRADATION STUDIES PERFORMED ON

TRIS-PERFLUOROALKYLETHER-s-TRIAZINE, $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$

Temp. °C	Atm.	Starting Material Used	Recov	Oxygen Consumed		Products Formed				
						CO_2	CO	R_fCONH_2	R_fCN	R_fH
		mg	%[a]	mg	%[b]	%[a]	%[a]	%[a]	%[a]	%[a]
325	N_2/H_2O[c]	697.2	95.5	-	-	0.27	0.01	2.79	1.73	1.04
235	Air/Jet-A[d]	500.2	97.7	5.86	100	0.53	0.10	?	0.03	1.19

a) Weight percent of starting material. b) Percent of available oxygen. c) The quantity of water employed was 61.9 mg; it was essentially recovered. d) The quantity of Jet-A fuel employed was 1091.1 mg.

TABLE V

SUMMARY OF DEGRADATION STUDIES PERFORMED ON

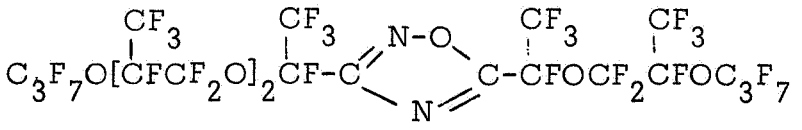
3,5-BIS(PERFLUORO-n-HEPTYL)-1,2,4-OXADIAZOLE

Temp. °C	Atm.	Starting Material Used	Recov	Oxygen Consumed		Products Formed				
						CO_2	CO	R_fCONH_2	R_fCN	R_fH
		mg	%[a]	mg	%[b]	%[a]	%[a]	%[a]	%[a]	%[a]
325	N_2/H_2O[c]	532.1	98.4	-	-	0.12	0.17	0.42	-	+[e]
235	Air/Jet-A[d]	832.2	72.9	5.9	100	0.27	0.04	6.63	1.01	1.71

a) Weight percent of starting material. b) Percent of available oxygen. c) The quantity of water employed was 53.2 mg. d) The quantity of Jet-A fuel employed was 847.0 mg. e) Present in small quantity.

TABLE VI

SUMMARY OF DEGRADATION STUDIES PERFORMED ON



Temp °C	Atm	Starting Material Used	Recov	Oxygen Consumed		Products Formed					
		mg	%[a]	mg	%[b]	SiF_4 %[a]	CO_2 %[a]	CO %[a]	$R_fOR_fCONH_2$ %[a]	R_fOR_fCN %[a]	R_fOR_fH %[a]
235	Air	813.1	98.8	0.5	10	0.20	0.41	-	-	0.2	0.2
235	Ar/H_2O[c]	708.9	98.8	-	-	-	0.31	-	Trace	+[f]	+[f]
235	Air/Jet-A[d]	896.1	92.3	5.6	100	-	0.20	0.04	0.39	1.13	0.73
325	N_2	693.0	99.4	-	-	0.02	0.07	-	-	Trace	Trace
325	Air	679.5	98.7	0.8	16	0.23	0.44	0.26	-	0.2	0.2
325	N_2/H_2O[e]	469.1	98.5	-	-	-	0.11	0.01	Trace	+[f]	+[f]

a) Weight percent of starting material. b) Percent of available oxygen. c) The quantity of water employed was 101.3 mg. d) The quantity of Jet-A employed was 920.2 mg. e) The quantity of water employed was 49.0 mg. f) Present in small quantity.

TABLE VII

SUMMARY OF DEGRADATION STUDIES PERFORMED ON

2,5-BIS(PERFLUORO-n-HEPTYL)-1,3,4-OXADIAZOLE

Temp. °C	Atm.	Starting Material Used	Recov	Oxygen Consumed		Products	
		mg	%[a]	mg	%[b]	mg	%[a]
235	Air-1	939.9	97.9	5.4	100	30.6	3.2
235	Air-2[c]	242.7	98.9	none	0	0.6	0.2
235	Argon/H_2O[d]	871.6	99.3	-	-	1.5[e]	0.2
325	Argon	834.1	99.5	-	-	1.2	0.1
325	Air[c]	1032.8	60.0[f]	54.2	99.6	348.0	33.7
325	Argon/H_2O[g]	930.5	99.8	-	-	2.6[e]	0.3

a) Percent of the weight of the starting material. b) Percent of oxygen available. c) This test was performed using 500 ml ampoule; oxygen available, 54.5 mg. d) In this test 84.1 mg of water was employed. e) In view of the water present this value is not very accurate. f) The involatile residue amounted to 69% of the oxadiazole originally taken; however, it contained 88% of the 1,3,4-oxadiazole admixed with material absorbing at 6.18 and 6.31 μ. g) In this test 80.6 mg of water was employed.

TABLE VIII

PRODUCTS FORMED ON THERMAL OXIDATIVE DEGRADATION

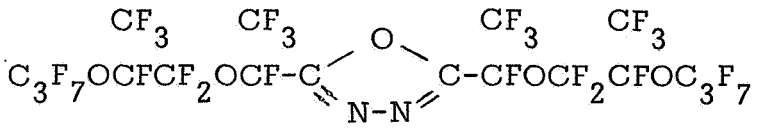
OF 2,5-BIS(PERFLUORO-n-HEPTYL)-1,3,4-OXADIAZOLE IN AIR

Product	235°C %[a,b]	325°C %[a]
CO	0.05	0.5
CO_2	0.49	9.9
SiF_4	0.36	10.3
COF_2	1.40	4.4
BF_3	?	0.7
$C_7F_{15}CN$	0.4	3.7
CF_4	T	T
Unidentified	0.5	10.1

a) Percent of starting material. b) The data are for the Air-1 test listed in Table VII.

TABLE IX

SUMMARY OF DEGRADATION STUDIES PERFORMED ON



Temp. °C	Atm.	Starting Material Used	Starting Material Recov.	Oxygen Consumed		Products	
		mg	%[a]	mg	%[b]	mg	%
235	Air	523.0	99.3	0.3	5.3	3.4	0.65
235	Ar/H_2O[c]	502.8	99.8	-	-	0.9	0.18
235	Air/Jet-A	635.5	97.3	5.8	100	2.0	0.31
325	N_2	586.2	99.2	-	-	4.3	0.73
325	Air	300.9	96.1	1.2	20.6	11.8	3.92

a) Percent of the weight of the starting material. b) Percent of oxygen available. c) In this test 61.7 mg of water was employed and it was quantitatively recovered.

TABLE X

PRODUCTS FORMED ON DEGRADATION OF

2,5-BIS(PERFLUOROALKYLETHER)-1,3,4-OXADIAZOLE

Compound	% [a] (235°C, Air)	% [a] (325°C, N_2)	% [a] (325°C, Air)	% [a] 235, Air/Jet-A [b]
CO	0.02	0.02	0.06	0.05
CO_2	0.21	0.03	1.25	0.08
SiF_4	0.02	0.01	1.23	?
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]OCF_3$?	-	-	0.07	?
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH_2$	0.02	T	0.02	T [c]
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$	0.25	0.29	0.49	0.02
$C_3F_7OCF(CF_3)CN$	T	T	T	T
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$	0.08	0.34	0.76	0.14
$C_3F_7OCF(CF_3)H$	T	T	0.06	0.15

a) Weight percent is based on weight of oxadiazole used. b) The typical products formed by the Jet-A itself when subjected to air at 235°C were found to be identical to those listed in Table II and are not included.
c) T = <0.0005% by weight.

TABLE XI

ION FRAGMENTS AND INTENSITIES RELATIVE TO THE BASE PEAK OF 1,2,4-OXADIAZOLES[a]

m/e	I[b]	II[c]	III[d]	m/e	I[b]	II[c]	III[d]
69	74.8	70.0	59.1	237		3.1	
76		5.4		287			14.6
92	37.9			292		3.3	
97		10.6	9.7	335		15.7	13.5
100	13.3	12.3	6.9	453			7.2
119	33.1	21.9	19.9	487	100		
126		36.0	4.2	488	17.4		
131	27.3	5.8		501		3.4	3.5
142		8.6	3.0	537		21.2	
147		19.4	18.1	619			14.5
150		11.5	7.7	703		5.1	
169	24.3	100	100	785			7.4
170		4.2	3.7	787	27.1		
181	5.6			788	6.0		
192		7.4		951			4.5
219	5.3			985		4.5	
				1035		3.9	

a) Peaks having relative intensities less than 3% of the base peak and lower than m/e 69 are not reported. b) Compound I is 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole. c) Compound II is 3-perfluoroalkylether-5-perfluoro-n-heptyl-1,2,4-oxadiazole. d) Compound III is 3,5-bis(perfluoroalkylether)-1,2,4-oxadiazole.

TABLE XII

ION FRAGMENTS AND INTENSITIES RELATIVE TO THE BASE PEAK OF 1,3,4-OXADIAZOLES[a]

m/e	IV[b]	V[c]	VI[d]	m/e	IV[b]	V[c]	VI[d]
69	100.0	97.6	81.9	437	17.8	3.8	
71	3.3			459	5.8		
76	7.5	3.0	3.0	487	95.2		
78	5.1			488	20.0		
81	3.6			519		3.0	3.0
90	5.1			537		21.4	
92	10.4	4.0	3.0	538		3.2	
93	10.7	4.5		569		27.1	
97		6.9	8.0	570		4.3	
100	23.6	14.3	12.9	619			19.7
109	36.7	5.6	1.2	703		9.1	
112	3.8			709	4.3		
119	74.6	37.9	34.8	769		6.0	
126		4.9	6.7	785			10.1
128		2.0	3.5	787	39.3		
131	56.3	15.7	3.5	788	8.0		
143	3.6			806	3.2		
147		16.6	13.9	819		25.3	
150		6.1	7.4	820		5.6	
159	4.5	7.2		851			7.0
169	61.9	100.0	100.0	869		32.4	
170		5.7	4.8	870		6.2	
181	15.0	6.3		888		1.1	
219	11.0	3.4		901			31.9
231	6.5			902			7.0
281	8.7	3.2		951			15.1
335		22.0	27.6	952			3.3
369	19.8	10.6		970			0.1
403		7.4					

a) Peaks having relative intensities less than 3% of the base peak and lower than m/e 69 are not reported. b) Compound IV is 2,5-bis(perfluoro-n-heptyl)-1,3,4-oxadiazole. c) Compound V is 2-perfluoro-n-heptyl-5-perfluoroalkylether-1,3,4-oxadiazole. d) Compound VI is 2,5-bis(perfluoroalkylether)-1,3,4-oxadiazole.